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Magnetic filler alignment of paramagnetic Fe_3O_4 coated SiC/epoxy composite for thermal conductivity improvement

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Abstract

We fabricated vertically aligned silicon carbide (SiC)/epoxy composites along the direction of heat transport using a magnetic field. SiC was made magnetically responsive by introduction of strong paramagnetic iron oxide (Fe_3O_4) nanospheres, and the amount of iron oxide deposited is easily controlled by modulating the precursors. Fe_3O_4-coated SiC filler was vertically aligned by an external magnetic field and generated particle columns. These columns act as a superior thermal conducting path. The thermal conductivity of the synthesized vertically aligned composite increased from 0.945 W m^{-1} K^{-1} to 1.681 W m^{-1} K^{-1} with 20 vol% filler loading that is a 1.78-fold increase compared with the randomly dispersed filler composite. Moreover, the electrical conductivity of SiC, which is a major drawback, was also controlled by the electrically insulating iron oxide coating. These results suggest promising applications of magnetically aligned SiC-based polymer composites in thermal interface materials.

Keywords: B. Composites; C. Thermal properties; C. Magentic properties; D. SiC; Vertical alignment

1. Introduction

Microelectronic packaging is playing an increasingly important role in the advancement of electronic and electrical technologies as electronic devices, communication equipment, and lighting apparatus become ever denser and more powerful [1,2]. With the miniaturization of electronic devices, heat dissipation has emerged as a critical problem that affects the device performance and reliability, especially in high power devices such as high power diode lasers, high-brightness light emitting diodes, and high power transistors. It is well known that the reliability of an electronic device is exponentially dependent on the operating temperature of the junction, whereby a small difference in the operating temperature can result in a two-fold reduction in the lifespan of a device [3]. To ensure proper device operation, the unwanted heat must be removed as quickly and effectively as possible to maintain the operating temperature, suggesting that the packaging materials of the product need to have good thermal conductivity [4].

In typical flip-chip assemblies of microprocessors, heat spreaders and heat sinks with high thermal conductivities have been employed to dissipate the heat generated in the die. However, the surface asperities greatly limit the actual contact between the solid surfaces (e.g. die/heat spreader and heat spreader/heat sink), thereby reducing the effective thermal conduction [5]. The remaining area is separated by an insulating air gap (thermal conductivity of air = 0.0242 W m^{-1} K^{-1}) of varying thicknesses. Therefore, thermal interface materials (TIMs) are introduced to fill the gap between the asperities in order to minimize the thermal contact resistance, and extensive research has been conducted to develop novel, improved TIMs [6]. TIMs have to be mechanical stable, reliable, nontoxic, low-cost, and easy to apply. They should

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possess as high thermal conductivity as possible, as well as low coefficient of thermal expansion. In order to enhance the thermal conductivity, many kinds of composite particles, such as metals, ceramics, and nanostructured carbon materials have been applied to thermosetting or thermoplastic polymers to form composite TIMs [7–9].

Generally, extremely high filler loading, typically larger than 50 vol%, is required to achieve high thermal conductivity when these conventional composite fabrication methods are used. However, one of the major drawbacks of composites with such high filler loading is the degradation of the mechanical properties of the polymer, with the rigid (typically ceramic) filler particles acting as defects in the polymer matrix [10]. Moreover, these high filler loadings reduce the processability of the material—one of the major advantages of polymers—because the viscosity of the composite increases with the filler volume fraction. In order to achieve both high thermal conductivities and reasonable mechanical properties, a novel approach based on low filler loading is required.

Recently, particle alignment has been shown in a variety of industrial applications, notably in biology, microfluidics, and electronics [11,12]. Xu et al. achieved directly synthesized carbon nanotube (CNT) arrays on a silicon wafer using plasma-enhanced chemical vapor deposition and greatly reduced the thermal interface resistance [13]. Huang et al. also synthesized carbon nanotube arrays according to the heat transfer direction and achieved a two-fold higher thermal conductivity compared to a dispersed CNT composite at 0.4 vol% CNT [14]. However, this procedure is not suitable for compounding because of prohibitive manufacturing costs and the thermal damage inflicted on the composite at high temperatures. Yoshihara et al. achieved molecular orientation along the injection direction and studied its effect on thermal conductivity [15]. However, this method is not broadly applicable because of the very particular synthesis method, namely extrusion from a processable melt mix thermoplastic matrix. Although extrusion is a widely used compounding method, it has several drawbacks, two major ones being limited filler content and particle breakage. Indeed, because of the very high shear forces generated in the process, relatively soft particles can be damaged and cracked. Furthermore, the method described cannot produce true particle arrays because their alignment is fixed to the injection direction.

Among the different particle array methods, magnetic field alignment is particularly attractive in this regard since the external magnetic field not only provides total control over the alignment direction, but also because the procedure is inexpensive and does not damage the composite. In this study, we synthesized a magnetic SiC hybrid particle decorated with iron oxide (magnetite) nanospheres. Thermally conductive composites using SiC have been also reported, and SiC is a very attractive, thermally conducting filler material because of its high thermal conductivity, low coefficient of thermal expansion, and commercial price [16]. Unfortunately, SiC is a good electric conductor, which is one of the drawbacks for TIM applications because that can cause short circuits. Therefore, to adapt the SiC particle for use as a thermal conducting particle, surface modification was needed. Moreover, magnetic alignment requires the filler to respond to the external magnetic field. Although SiC is not an intrinsically magnetic material, magnetically responsive SiC can be prepared by surface modification using paramagnetic iron oxide nanoparticles. Iron oxide nanoparticles interact with poly(vinyl pyrrolidone) (PVP)-coated SiC surfaces through electrostatic interactions between the positively charged nanoparticles and the negatively charged SiC [17]. The electrical conductivity problem was also controlled by introduction of electrically insulating iron oxide particles. This magnetically actuatable SiC is the tool that will allow the filler alignment to be manipulated through the magnetic field.

2. Experimental section

2.1. Synthesis of Fe_3O_4-decorated SiC

The residual SiO_2 layer adsorbed on the surface of the SiC particles was removed by treatment with hydrofluoric acid (HF). In a typical synthesis, 120 g of SiC powder (hereafter, Raw SiC) was placed in 300 mL of 10% HF solution and stirred for 24 h. Subsequently the sample was leached with distilled water until the pH of the leaching water reached 7–8. These samples were denoted as SiC–HF. In order to introduce the oxygen-containing functional groups on the SiC surface, HF-treated SiC powder was dispersed in a 34% hydrogen peroxide (H_2O_2) solution and heated to 85 °C for 24 h with vigorous stirring. The resulting mixture was filtered, washed several times, and dried in a vacuum oven at 60 °C for 24 h. The hydrogen peroxide treatment of HF-treated silicon carbide provides the oxygen-containing functional groups that help to entangle the PVP. Detailed information of the SiC surface modification was reported in our previous study.

Iron oxide nanoparticles were synthesized on the surface-modified SiC by hydrolysis of an aqueous solution. First, 1.5 g of PVP was dissolved in 100 mL ethanol and 1 g of SiC powder was added with mechanical stirring to homogenize the aqueous dispersion. A few hours later, a certain amount (see Table 1) of $FeCl_3 \cdot 6H_2O$ was added into the SiC dispersion, which was then stirred at 90 °C overnight. Next, 20 mL hydrazine hydrate solution was added and the mixture stirred for 4 h at 90 °C. Finally, the products were washed with ethanol, filtered several times, and vacuum-dried at 80 °C for 5 h to remove the solvent. Magnetite nanoparticles were synthesized by chemical precipitation of Fe^{3+} ions. After the

Table 1
The amount of iron salt and density of SiC, Fe_3O_4, and various SiC–Fe_3O_4 particles.

	$FeCl_3 \cdot 6H_2O$ [g/1 g of SiC]	Density [g/cm^3]
Raw SiC		3.21
SiC–Fe_3O_4 (0.1)	0.3502	3.33
SiC–Fe_3O_4 (0.5)	0.7004	3.47
SiC–Fe_3O_4 (1)	3.5022	3.64
SiC–Fe_3O_4 (1.5)	5.2534	3.63
Raw Fe_3O_4		5